Preparation of $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$: A Metallo Derivative of Hexaborane(10)

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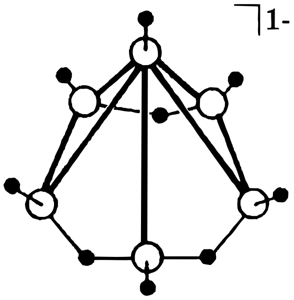
Introduction

The $[B_6H_9]^-$ ion is generated through removal of a proton from a basal B−H−B bond of the B_6H_{10} molecule (eq 1).[1] The

$$B_6H_{10} + KH \rightarrow K[B_6H_9] + H_2 \qquad (1)$$

structure of the resulting anion is that of a pentagonal pyramid with three B−H−B and two B−B bonds in its base. The B−B bonds are susceptible to insertion of electrophiles.[2] Edge-bridged derivatives of $[B_6H_9]^-$ have been prepared through insertion of BH_3[3] and metal cations[4] into these basal B−B bonds. Reports of the metal derivative chemistry of $[B_6H_9]^-$ have been principally concerned with main group metals Mg,[4a] Zn,[4a] Cd,[4a] Al,[4b] Cu,[4c,d] and Sn.[4e] While the transition metals Fe[5] and Pt[6] have also been inserted into a basal B−B site of the B_6 framework, derivatives of $[B_6H_9]^-$ containing the early transition metals are unreported. Presented here are the results of our study of the formation and properties of a Ti(III) derivative of $[B_6H_9]^-$.



Results and Discussion

The title complex was prepared as a blue, air-sensitive crystalline solid according to eq 2.

$$2K[B_6H_9] + 2(\eta^5\text{-}C_5H_5)_2TiCl \rightarrow [(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2 + 2KCl \quad (2)$$

Crystals suitable for X-ray analysis could not be obtained. Elemental analyses and the mass spectrum are consistent with the formula $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]$. The three most intense peaks in the parent envelope are at m/e = 251, 252, and 253 (calcd for $C_{10}H_{19}TiB_6$ m/e = 253). However, the molecular weight in benzene solution by freezing point depression indicates the existence of a dimeric species, $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$ (obsd 535 g/mol, calcd 504 g/mol). B_6H_{10} is regenerated in 86% yield from the reaction of $[(\eta^5\text{-}C_5H_5)_2\text{-}TiB_6H_9]_2$ with HCl in $(CH_3)_2O$ at −97 °C. This result suggests that the Ti is bound to the B_6 cage in a basal edge-bridging site, since treatment of the basal edge-bridged complex 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$[4c,d] with HCl affords B_5H_9, whereas the complex 2-Mn-$(CO)_5B_5H_8$ with the metal at a terminal basal site does not generate B_5H_9 when it is treated with HCl.[7] The proposed structure of $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$ is shown in Figure 1. It contains two equivalent $(\eta^5\text{-}C_5H_5)_2Ti$ units coordinated to two B_6H_6 clusters through basal edge B−Ti−B bonds. This structure resembles that of $[Pt_2(B_6H_9)_2(PMe_2Ph_2)_2]$, except that the platinum complex has a direct metal−metal[6] bond while ESR spectra do not support Ti−Ti interaction in the title complex. The title compound is dark blue in color. It is thermally stable *in vacuo* to about 100 °C, but it is extremely oxygen and water sensitive. It turns yellow/orange when it is exposed to air. It sublimes *in vacuo* at about 100 °C. Some decomposition occurs on sublimation between 100 and 125 °C as indicated by the appearance of traces of $(\eta^5\text{-}C_5H_5)_2TiBH_4$[8] in the sublimate. It melts at 123 °C with decomposition. It is soluble in $(CH_3)_2O$, $(C_2H_5)_2O$, THF, benzene, and toluene. It reacts with chlorinated solvents such as $CHCl_3$ and CH_2Cl_2.

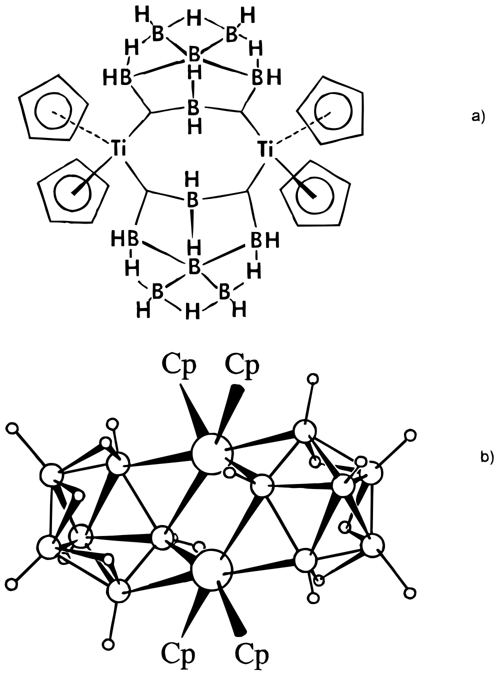


Figure 1. (a) Proposed topological and (b) molecular structure of $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$.

The ^{11}B NMR spectrum at 80.253 MHz in toluene at 25 °C consists of two featureless signals centered at 31.6 and −21.7 ppm, with an area ratio of ca. 2:1 (Figure 2). Assignments in this spectrum are based upon the proposed dimeric structure. The signal at 31.6 ppm is assigned to the two basal boron atoms that are not connected to Ti. The signal at −21.7 ppm is assigned to the apical boron atom. It is assumed that the boron

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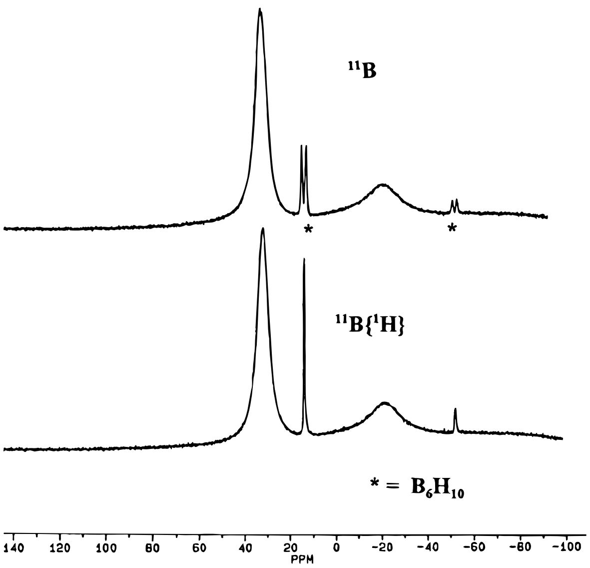

Figure 2. ^{11}B NMR spectra of $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$.

atoms attached to one titanium and the boron atom attached to both titaniums have signals that are broadened into the base line and are not observed. Note that the ^{11}B[^{1}H] NMR spectrum is virtually indistinguishable from the normal ^{11}B NMR spectrum (Figure 2). The broad decoupled nature of the ^{11}B NMR signals and the large downfield shifts of the ^{11}B signals of $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$ compared to those of B_6H_{10} are indicative of paramagnetic broadening by the formally 17-electron Ti(III) center.[9] Similar broadening and contact and pseudocontact shifts in resonances have been previously observed for carborane and metalloborane complexes of Fe(III), Mn(III), and Cr(III).[10] ^{1}H NMR signals assignable to hydrogens bound to boron were not observed. Proton signals were not observed, presumably due to paramagnetic broadening. ESR spectra in benzene and also in THF at 25 °C consist of only a single symmetrical signal at $g = 1.9786$ and 1.9780, respectively. The solid state ESR spectrum at 25 °C exhibits symmetry characteristic of three overlapping resonances due to an anisotropic electronic environment surrounding the Ti center. The three values are $g_1 = 1.9864$, $g_2 = 1.9797$, and $g_3 = 1.9685$, with an average value of $g = 1.9782$. These spectra suggest that there is no electronic interaction[11] between the two 17-electron Ti(III) centers in $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$.

Experimental Section

All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of pure dry N_2. Tetrahydrofuran (THF) was dried over sodium−benzophenone ketyl and stored in a Pyrex flask equipped with a Teflon stopcock. Toluene and benzene were dried and stored over sodium slivers in Pyrex bulbs. $K[B_6H_9]$ was prepared by published procedures[1] using hexaborane(10) also produced from a published procedure.[12] KH was obtained from Strem Chemicals. $(\eta^5\text{-}C_5H_5)_2TiCl$ was purchased from Aldrich Chemicals and sublimed *in vacuo* prior to use.

^{11}B NMR spectra ($\delta(BF_3OEt_2) = 0.00$ ppm) were collected on a Bruker AM 250 NMR spectrometer at 80.253 MHz. IR spectra were obtained on a Mattson Polaris spectrometer. ESR spectra were obtained on a Varian E-Line, E-12 spectrometer. The crysocopic molecular weight was determined on an apparatus designed and constructed in this laboratory.[13] Analyses were performed by Schwartzkopf Microanalytical Laboratories.

Synthesis of $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$. In a typical reaction, 4.00 mmol (0.854 g) of $(\eta^5\text{-}C_5H_5)_2TiCl$ was added to a solution of 4.0 mmol (0.45 g) of $K[B_6H_9]$ in 5.0 mL of THF at −78 °C on the vacuum line in an extractor suitable for low-temperature filtration. The materials had previously been loaded into the extractor in a drybox which was rigorously free of O_2. A portion of the $(\eta^5\text{-}C_5H_5)_2TiCl$ dissolved leaving a green solution. The solution was warmed to 0 °C, and a blue solid formed. The solution was stirred for 3 h, at which time an additional 5.0 mL of THF was condensed into the reaction vessel. The solution was frozen and the extractor inverted and cooled to −78 °C to filter the solution as it melted. The blue solid collected on the frit was washed repeatedly with THF at −78 °C. In the drybox, a clean receiver bulb was placed on the extractor, and the apparatus was returned to the vacuum line and evacuated. THF was added to the blue solid at 0 °C, and the product was washed through the frit to the receiver, leaving white KCl on the frit. Slow evaporation of the THF resulted in large blue crystals of the product. The product was further purified in a separate vessel by fractional crystallization. The product was extremely air and moisture sensitive. It sublimed at 100 °C *in vacuo* with decomposition and melted at 123 °C. Anal. (Ti:B:C:H) found, 1.00:1.356:2.495:0.413; calcd, 1.00:1.354:2.507:0.400. The analytical sample contained 1.43% KCl. The infrared spectrum in Nujol and Fluorolube in cm^{-1} (I): 3100 (m), 2585 (m), 2565 (m), 2530 (s), 2515 (s), 2400 (w), 2290 (w), 1890 (w, br), 1840 (vw, br), 1745 (w, br), 1650 (w, br), 1435 (m), 1324 (m), 1060 (w), 1010 (s), 955 (w), 913 (w), 812 (vs), 738 (m), 715 (m), 675 (w), 630 (m), 608 (m), 588 (m), 417 (m), 378 (m). X-ray powder pattern (Cu Kα), d (I): 8.76 (s), 6.69 (vs), 6.26 (m), 5.91 (s), 5.01 (m), 4.76 (vw), 4.46 (vw), 4.32 (vw), 4.19 (m), 4.01 (vw), 3.90 (w), 3.66 (w).

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